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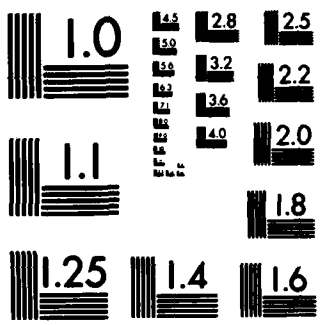

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| 4. TITLE (and Subtitle): Hartree-Fock interaction between a helium Atom and Lithium-metal: A test for the effective Medium theory | | 5. TYPE OF REPORT & PERIOD COVERED: Interim<br>6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s): B. K. Rao, P. Jena, D. Schillady, A. Hintermann and M. Manninen | | 8. CONTRACT OR GRANT NUMBER(s): N00014-82-K-0576 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS: Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, N.Y. 14853 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS |
| 11. CONTROLLING OFFICE NAME AND ADDRESS | | 12. REPORT DATE: February 11, 1985<br>13. NUMBER OF PAGES: 12 |
| 14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) | | 15. SECURITY CLASS. (of this report): Unclassified<br>15a. DECLASSIFICATION/ DOWNGRADING SCHEDULE |

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The interaction of a helium atom with 6 and 10 atom clusters of lithium has been calculated using the unrestricted Hartree-Fock method, Hartree-Fock method with correlation corrections, and the effective medium theory. Inside the cluster the helium embedding energy is found to be proportional to the electron density of the cluster. The proportionality constant obtained by the Hartree-Fock method is in fair agreement with that calculated in the homogeneous electron gas using the local density approximation. Outside the cluster, in the region compatible with the helium diffraction experiments, the self-consistent calculations give much larger repulsion than

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# Hartree-Fock interaction between a helium atom and lithium metal: a test for the effective medium theory

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## Abstract

The interaction of a helium atom with 6 and 10 atom clusters of lithium has been calculated using the unrestricted Hartree-Fock method, Hartree-Fock method with correlation corrections, and the effective medium theory. Inside the cluster the helium embedding energy is found to be proportional to the electron density of the cluster. The proportionality constant obtained by the Hartree-Fock method is in fair agreement with that calculated in the homogeneous electron gas using the local density approximation. Outside the cluster, in the region compatible with the helium diffraction experiments, the self-consistent calculations give much larger repulsion than the effective medium theory.

The utilization of helium diffraction for detailed structural studies of surfaces requires a method for linking the scattering potential to the structure. A fully self-consistent calculation of the potential energy of the helium atom outside a semi-infinite metal surface has been so far, too complicated to accomplish but several theoretical or semiempirical approaches have been suggested for determining the scattering potential[1-7]. All these approaches give the result that the helium potential energy is roughly proportional to the unperturbed electron density at the surface. This relationship comes as a natural result of the so-called effective medium[8] or quasiatom[9] theory which calculates the impurity binding energy as a functional of the electron density of the host. The leading repulsive term of the scattering potential can be written as[6,10]

$$V(\vec{r}) = \alpha_{eff}\bar{n}(\vec{r}) \tag{1}$$

where $\alpha_{eff}$ is a constant and $\bar{n}(\vec{r})$ is the average of the host electron density over the electrostatic potential of the helium atom. It turns out that outside a metal surface as well as inside the metal $\bar{n}(\vec{r})$ is, within a good occuracy, proportional to $n(\vec{r})$, the <u>local</u> host electron density at the helium site. Then approximately

$$V(\vec{r}) = \bar{\alpha}_{eff}n(\vec{r}) \tag{2}$$

where $\bar{\alpha}_{eff}$ is a new constant.[6]

The effective medium theory has been tested by model calculations. The helium trappling energies in jellium vacancies, and the helium potential energy outside a jellium surface calculated by the effective

medium theory agree well with fully self-consistent calculations.[9,10] Also, the calculated helium trapping energies in real metal vacancies agree well with experimental results[11,12]. When applied to helium diffraction the effective medium theory gives qualitatively the correct features of the potential[2] but fails to give the corrugation of the potential quantitatively correctly.[13]

In this letter we report on self-consistent Hartree-Fock cluster calculations for He-Li interaction and compare the results with those of the effective medium theory. We show that inside the metal the effective medium theory gives good results whereas outside the cluster, in the region where the helium scattering takes place, the self-consistent Hartree-Fock potential is more repulsive than the prediction of the effective medium theory.

The two Li clusters considered are shown in Fig. 1. The helium atom was moved from the octahedral interstitial site outside the cluster as indicated in the figure, and self-consistent total energy calculations were performed for several helium sites along that line. The computations for the cluster with 6 lithium atoms were repeated using several different sets of basis functions[14,15] to make sure that the choice of basis sets did not introduce any uncertainties. For testing the sensitivity of the results on the cluster size a calculation has also been made for a cluster with ten lithium atoms. In the best calculation using the 6-31G basis[14,15] the effect of correlation was included by a perturbative technique (so called MP2)[19,20]. Using the same basis set we also calculated the He-He potential and found a good agreement with earlier calculations.[16]

The results of the self-consistent calculations are shown in Fig. 2 together with the result of the effective medium theory, Eq. (1). The

results computed using different basis sets show that inside the cluster the helium energy depends slightly on the basis set used whereas outside the cluster the difference becomes smaller. The correlation correction lowers the helium energy by about 2% in the center of the cluster and at the distance of 8 a.u. about 7%. The cluster calculations of the impurity energy often show sensitivity on the clusters size[17] and geometry[18]. To check the dependence of the helium energy on the cluster size we have repeated one calculation by adding 4 Li atoms in the 6 atomic cluster as shown in Fig. 1. These additional atoms change the helium potential inside the cluster but do not have a noticeable effect outside the cluster.

The result of the effective medium theory was calculated using the self-consistent Hartree-Fock electron density (Li 4-31g basis set) and the coefficient[6] $\alpha_{eff}=196 eV/a_0^3$ in Eq. (1). In the case of Li since the averaged density $\bar{n}(\vec{r})$ is within 3% of the local density $n(\vec{r})$ in all helium sites, we can use approximation

$$\bar{\alpha}_{eff} \approx \alpha_{eff}. \qquad (3)$$

which is valid only for Li and not necessarily for any other metal. Figure 2 shows that the effective medium theory describes the interaction of the helium atom within the Li cluster qualitatively correctly.

Using Eq. (2) we can determine the coefficient $\bar{\alpha}_{eff}$ once the self-consistent total energy and electron density are known. In Fig. 3 $\bar{\alpha}_{eff}$ determined from the Hartree-Fock results is shown as a function of the helium position. The effective medium theory predicts that $\bar{\alpha}_{eff}$ is nearly constant. The Hartree-Fock result for $\bar{\alpha}_{eff}$ is nearly constant

inside the metal and only slightly larger than that obtained for a homogeneous electron gas. However, outside the cluster where the electron density becomes small $\bar{\alpha}_{eff}$ increases rapidly. At a helium distance of 8 au. which corresponds to a typical helium scattering distance, the Hartree-Fock calculation already gives 3 times more repulsive potential than the effective medium theory. This is in accordance with the experimental findings that the actual scattering potential is much less corrugated than the result of the effective medium theory[5,13], suggesting that the scattering occurs further from the surface.

There are two possibilities why the effective medium theory is incapable of describing correctly the repulsion at large distances: either the nonlocal treatment of the exchange-correlation energy becomes important or the higher order corrections of the effective medium theory can not be neglected. The model calculation of Lang and Norskov[10] for jellium seems to indicate that the higher order corrections are small, but this is not necessarily the case at actual metal surfaces where the Freidel oscillations induced by the helium atom will overlap with the strong ion core potentials. In any case, it seems that the effective medium theory in its present form is incapable of calculating quantitatively correctly the helium potential in the region relevant to the diffraction experiments.

In conclusion, we have performed unrestricted Hartree-Foch calculations (including correlation corrections) for the interaction potential between a helium atom and a 6 atom cluster of lithium. Inside the cluster the potential is roughly proportional to the self-consistent electron density of the lithium cluster in accordance with the effective medium theory, but outside the cluster the potential is much more repulsive than predicted by the effective medium theory.

## Acknowledgements

Discussions with J. K. Norskov, T. Rantala, C. Umrigar and J. W. Wilkins are gratefully acknowledged. This work was supported in part by grants from Thomas F. Jeffress and Kate Miller Jeffress Foundation, National Science Foundation, Academy of Finland, and by The Petroleum Research Fund, administered by the ACS.

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## Figure Captions

Figure 1. Structure of the 6 and 10 atomic lithium clusters considered. Black dots show the 6 atomic BCC octahedron and the open circles the additional atoms in the 10 atomic cluster. The helium atom is moved along the heavy solid line.

Figure 2. Potentials between the He atom and the 6 and 10 atomic Li clusters. The Li atom basic set is denoted for each curve. EMT is the result of the effective medium theory.

Figure 3. The proportionality coefficient $\bar{\alpha}_{eff}$ of Eq. (2) determined from the Hartree-Fock result (4-31g basis) EMT is the result calculated for a homogeneous electron gas[6].

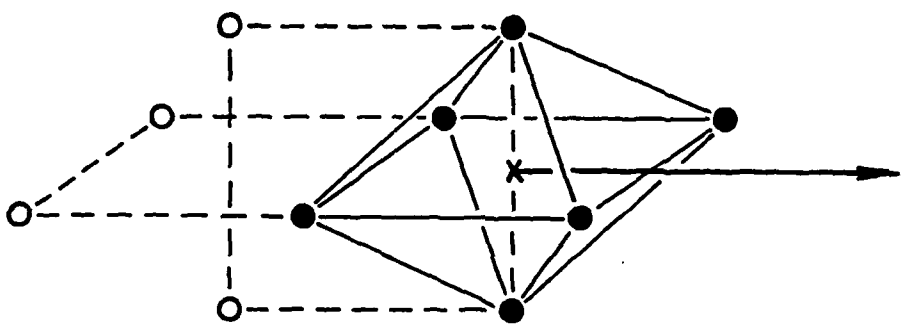

Figure 1

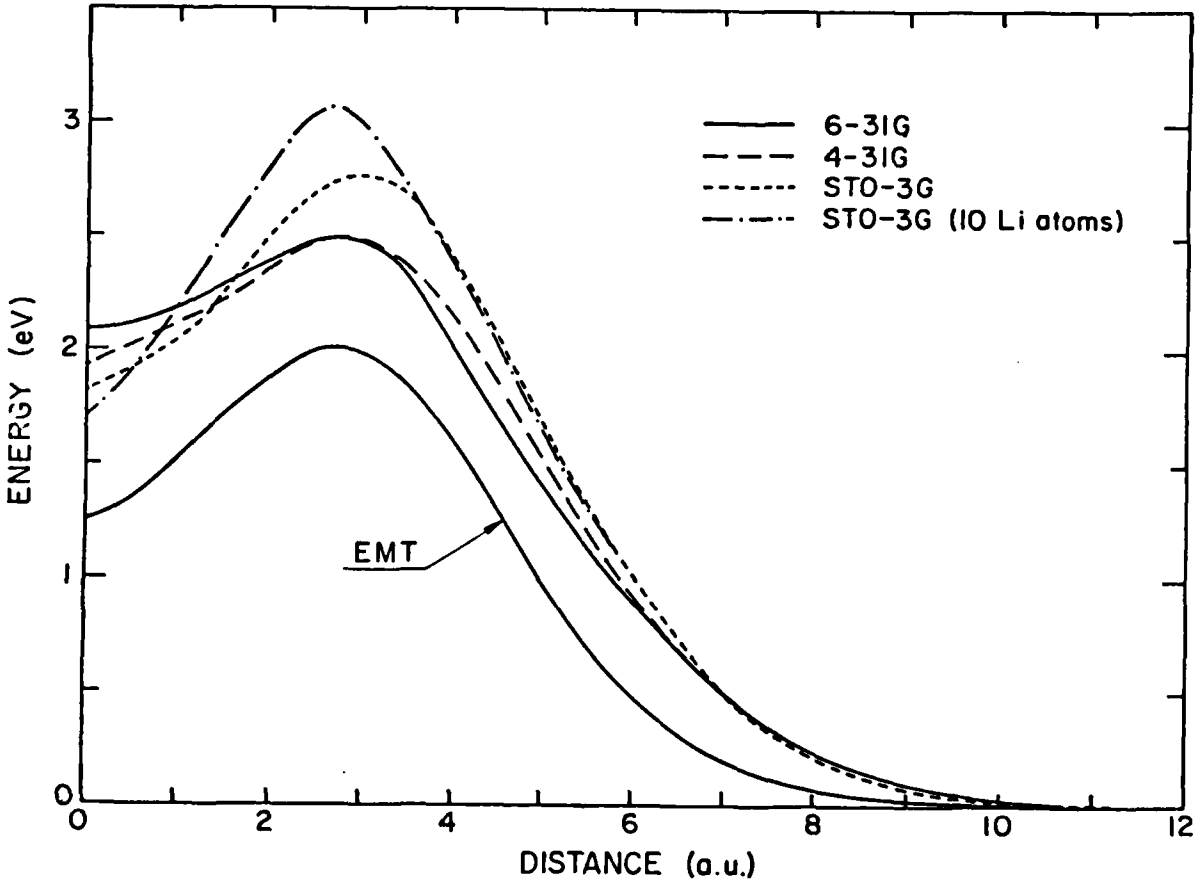
6-31G
4-31G
STO-3G
STO-3G (10 Li atoms)
EMT
ENERGY (eV)
DISTANCE (a.u.)
0
1
2
3
0
2
4
6
8
10
12

Figure 2

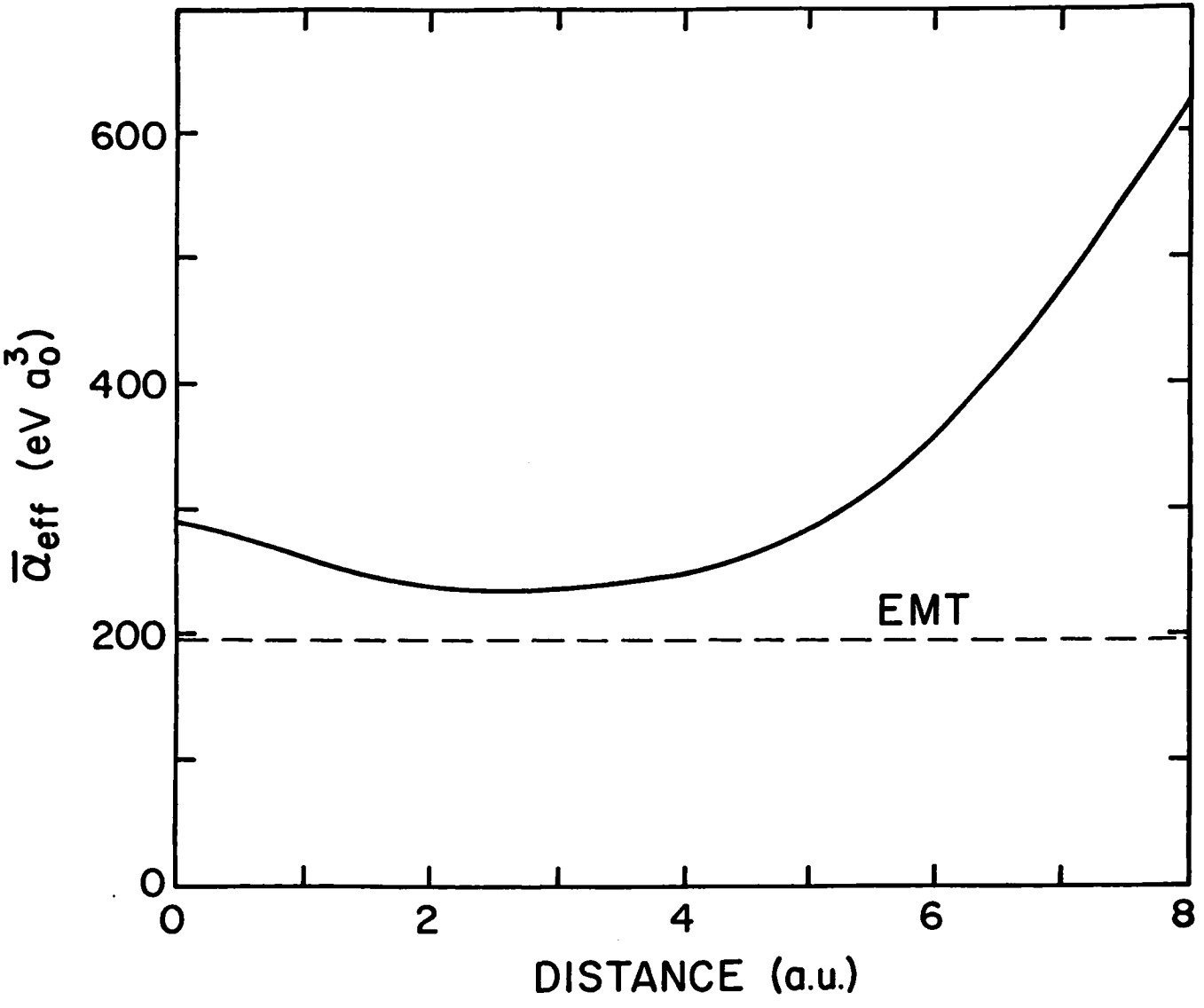


Figure 3

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